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(71) Applicant: Montedison S.p.A.
31, Foro Buonaparte
I-20121 Milan(IT)

(72) Inventor: Cuffiani, Illaro
33, via Bagaro
Ferrara(IT)

(72) Inventor: Galli, Paolo
106, viale Po
Ferrara(IT)

(72) Inventor: Zucchini, Umberto
11, via Leopardi
Ferrara(IT)

(74) Representative: Zumstein, Fritz, Dr. Dr. F. Zumstein sen. Dr. E. Assmann et al,
Dr. R. Koenigsberger Dr. F. Zumstein jun. Dipl.-Ing. F. Klingseisen Bräuhausstrasse 4
D-8000 München 2(DE)

(54) Catalyst components for polymerizing ethylene.

(57) Components of catalysts for polymerizing ethylene and the mixture of ethylene with alpha-olefins comprising the reaction product of (A) a magnesium compound, as Mg-chloride, Mg-alcoholate or a Grignard compound, with (B) a titanium, vanadium or zirconium compound having at least 2 metal-oxygen bonds, as a tetra-alcoholate, and with (C) a halogenated compound of metals of B, as Ti-tetrachloride.

According to an aspect of the invention, the reaction product (A) + (B), before being reacted with (C), is treated with a silicium compound having a halogenating and/or reducing action.

The catalysts according to the invention are suitable for obtaining ethylene polymers having a broad distribution of molecular weights.

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TITLE

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This invention refers to components of catalysts for polymerizing ethylene.

In particular it refers to components of catalysts which permit to polymerize, with high yields ethylene or mixtures thereof with up to 20%, referred to the total, of a higher alpha-olefin, such as propylene, to polymers having a broad distribution of molecular weights.

Examples of catalyst systems for the polymerization of ethylene or mixtures thereof with higher alpha-olefins are described in several patents, and the polymers obtained show a rather narrow distribution of molecular weights. Said polymers are suitable for injection molding and for other applications but are not useful for the manufacturing of articles by extrusion or blowing. In fact it is known that, due to the narrow distribution of the molecular weights, the polymers subject to breaking phenomena of the molten mass during the forming process and, furthermore, the articles prepared according to the above-mentioned techniques present knurlings.

In practice, the value of the ratio MI N/MI E is assumed; as a measure of the breadth of the molecular weight distribution, MI N and MI E are the melt indexes of the polymer measured at 190 °C with a weight of 1000 Kg and of 2.16 Kg respectively (ASTM D 1238). Polymers with about the same va

lue of melt index MI E have broader molecular weight distribution if the value of the MI N is higher.

Different methods can be used in order to obtain polymers with a rather broad molecular weight distribution. The simplest consists in suitably modifying the catalyst system, but such method often involves several drawbacks, such as for example, an excessive decreasing of the catalyst activity and/or difficulties in the regulation of the molecular weight of polymers.

The Applicant has now surprisingly found new components of catalysts for polymerizing ethylene which have high activity and permit to obtain ethylene polymers having a broad distribution of molecular weights without presenting the disadvantages mentioned hereinbefore. Such catalyst components are characterized by a high titanium content and by a low chlorine content.

The catalyst components forming the object of the present invention comprise the product obtained by reacting :

(A) a magnesium compound selected from

1) compounds of formula: $X_nMg(OR)_{2-n}$

wherein X is Cl or Br, a group -OH, an alkyl, aryl or a cycloalkyl having 1 to 20 carbon atoms; R is an alkyl, an aryl or a cycloalkyl having 1 to 20 carbon atoms, or a group -COR' in which R' is a hydrocarbon radical equal to R; $0 \leq n \leq 2$

compound (C) may be employed as such or diluted in a solvent like the ones indicated for the reaction between (A) and (B).

According to an embodiment, prior to the treatment with compound (C), the reaction product of (A) with (B) is reacted with a silicium compound capable of a halogenating action or a reducing action or a halogenating and simultaneously reducing action on compound B. Silicium halides, preferably silicium chlorides, or Si-hydrides and compounds containing atoms of halogen and hydrogen directly bound to a silicium atom are suitable to this purpose. Examples of such compounds are: $SiCl_4$, Si_4Cl_{10}, Si_2OCl_6, $C_2H_5SiCl_3$, $Si(OC_2H_5)Cl_3$, Si_3H_8, polysilanes $(SiH)_x$ wherein x has a value of at least 2, $(C_6H_5)_3SiH$, $(C_2H_5O)_3SiH$, polyhydrosiloxanes containing the monomeric unit

$$-\overset{H}{\underset{R}{\overset{|}{\underset{|}{Si}}}}O-$$

, in which R is H, a halogen, an alkyl with 1 to 10 carbon atoms, an aryl, an alkoxyl, an aryloxyl or a carboxyl, and having a polymerization degree comprised between 2 and 1000, preferably between 3 and 100; as examples of such polyhydrosiloxanes are:
$(CH_3HSiO)_4$, $H_3Si-O-SiH_2-OSiH_3$ and the polymethylhydrosiloxane (PMHS) of formula $(CH_3)_3SiO\left[(CH_2)HSiO\right]_nSi(CH_3)_3$, wherein n has a value of about 35.

Examples of silicium compounds capable of exerting simultaneously a halogenating and a reducing action are the following: $SiHCl_3$, $Si\ H_2Cl_2$, $Si\ H_3Cl$, CH_3SiCl_2H and $C_2H_5Si\ Cl\ H_2$.
Of course, mixtures of two silicium compounds, one of which having only a halogenating action and the other only a reducing action can be used.

The silicium compounds exerting a halogenating action are capable of substituting at least a group -OR of compound (B) with a halogen atom.

The silicium compound is employed in such an amount as to have from 0.5 to 100, preferably from 1 to 30, gram atoms of halogen per gram atom of Ti, V or Zr and from 0.1 to 100, preferably from 0.5 to 20, gram equivalents of reducing agent per gram atom of Ti, V or Zr.

The reaction with the silicium compound is carried out at a temperature ranging from 20°C to 200 °C and, also in this case, the use of a hydrocarbon diluent is optional.

Catalyst components prepared by reacting compound (A) with compound (B) and by successively reacting the resulting product with one or more silicium compounds having a halogenating and a reducing action are described in Belgian patent No. 867,400, but the corresponding catalysts provide ethylene polymers having a narrow molecular weight distribution.

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In case of treatment with the silicium compound, such treatment can be carried out after the reaction of product of (A) with (B) with compound (C). Practically it is preferred to treat the reaction product of (A) with (B) with a silicium compound and then to react the resulting product with compound (C).

By suitably choosing the catalyst component preparation conditions it is possible to affect the distribution of the molecular weights.

The catalyst components of the present invention are employed in combination with a cocatalyst consisting of a metal-alkyl of a metal of Groups I, II or III of the Periodic System, preferably an Al-trialkyl.

The polymerization of ethylene and the mixtures thereof with alpha-olefins is carried out according to the known methods in liquid phase in presence of an inert hydrocarbon diluent or in gas phase.

The polymerization temperature is generally comprised between 40° and 120°C. Higher temperatures ranging for example between 150° and 300 °C can be used.

In the following examples, which are given to better illustrate this invention without being however a limitation thereof, the polymerization of ethylene was carried out as described in example 1, i.e. in 1000 cc of n-hexane containing 1.5 g of $Al(i\text{-}C_4H_9)_3$, at 75°C and at a pressure of 14 atm.,

for 4 hours; the partial pressures of hydrogen (for the regulation of molecular weight) and of ethylene are specified in the description of the examples.

Examples 1 to 4 (Table I) refer to catalyst components prepared by directly treating reaction product of $MgCl_2$ with Ti alcoholate with $TiCl_4$.

Examples A, B, C, D (Table II) are comparative examples that show that catalyst components obtained by reacting reaction products $MgCl_2$ + Ti alcoholate with silicium compounds provide polymers having a narrow molecular weight distribution (the MI N/MI E ratio is not higher than 8.5).

Furthermore, the catalyst components prepared in examples A and B are employed in examples 5 to 12.

Examples 5 to 14 (Table III) relate to catalyst components prepared according to the alternative method which uses silicium compounds.

EXAMPLE 1

2.4 g of anhydrous $MgCl_2$ were dissolved in 17 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$ by heating at 140 °C under stirring for 3 hours. The solution obtained was diluted with 45 cc of ISOPAR G and 95 g of $TiCl_4$ were added thereto in 90 minutes; the mixture was then heated at 135 °C under stirring for 2 hours. At the end the resulting solid product was isolated by filtration

at 60 °C and repeatedly washed with 50 cc of anhydrous n-hexane at room temperature till disappearance of the chlorine ions from the solvent. After drying under vacuum at 40 °C for 3 hours, a catalyst component containing 22.3% of Ti was obtained.

For the ethylene polymerization test, 1000 cc of anhydrous n-hexane, 1.5 g of $Al(i\text{-}C_4H_9)_3$ as cocatalyst and 0.0082 g of the above-mentioned catalyst components were introduced in the order into a stainless steeel 2.5-liter autoclave equipped with a stirrer. The autoclave was heated at 75°C and 3 hydrogen atmospheres with 10 ethylene atmospheres were introduced feeding continuously ethylene to maintain the total pressure at 14 atmospheres. After 4 hours the polymerization was interrupted. The polymer was isolated by filtration and then was dried.
The results of the polymerization test are reported in Table I.

EXAMPLE 2

4.75 g of anhydrous $MgCl_2$ and 23.0 g of $Ti(OC_2H_5)_4$ were added to 90 cc of ISOPAR G, whereupon the mixture was heated at 100 °C under stirring for 3 hours. 95 g of $TiCl_4$ were added in 90 minutes to the resulting solution which was heated at 135 °C under stirring for 2 hours. By filtration

for 4 hours; the partial pressures of hydrogen (for the regulation of molecular weight) and of ethylene are specified in the description of the examples.

Examples 1 to 4 (Table I) refer to catalyst components prepared by directly treating reaction product of $MgCl_2$ with Ti alcoholate with $TiCl_4$.

Examples A, B, C, D (Table II) are comparative examples that show that catalyst components obtained by reacting reaction products $MgCl_2$ + Ti alcoholate with silicium compounds provide polymers having a narrow molecular weight distribution (the MI N/MI E ratio is not higher than 8.5).

Furthermore, the catalyst components prepared in examples A and B are employed in examples 5 to 12.

Examples 5 to 14 (Table III) relate to catalyst components prepared according to the alternative method which uses silicium compounds.

EXAMPLE 1

2.4 g of anhydrous $MgCl_2$ were dissolved in 17 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$ by heating at 140 °C under stirring for 3 hours. The solution obtained was diluted with 45 cc of ISOPAR G and 95 g of $TiCl_4$ were added thereto in 90 minutes; the mixture was then heated at 135 °C under stirring for 2 hours. At the end the resulting solid product was isolated by filtration

at 60 °C and repeatedly washed with 50 cc of anhydrous n-hexane at room temperature till disappearance of the chlorine ions from the solvent. After drying under vacuum at 40 °C for 3 hours, a catalyst component containing 22.3% of Ti was obtained.

For the ethylene polymerization test, 1000 cc of anhydrous n-hexane, 1.5 g of $Al(i\text{-}C_4H_9)_3$ as cocatalyst and 0.0082 g of the above-mentioned catalyst components were introduced in the order into a stainless steeel 2.5-liter autoclave equipped with a stirrer. The autoclave was heated at 75°C and 3 hydrogen atmospheres with 10 ethylene atmospheres were introduced feeding continuously ethylene to maintain the total pressure at 14 atmospheres. After 4 hours the polymerization was interrupted. The polymer was isolated by filtration and then was dried.
The results of the polymerization test are reported in Table I.

EXAMPLE 2

4.75 g of anhydrous $MgCl_2$ and 23.0 g of $Ti(OC_2H_5)_4$ were added to 90 cc of ISOPAR G, whereupon the mixture was heated at 100 °C under stirring for 3 hours. 95 g of $TiCl_4$ were added in 90 minutes to the resulting solution which was heated at 135 °C under stirring for 2 hours. By filtration

at 60 °C a solid product was isolated which was repeatedly washed at room temperature with 50 cc of anhydrous n-hexane until thorough removal of free $TiCl_4$ from the product. The catalyst component so prepared, after drying under vacuum at 40 °C for 3 hours, contained 29.45% of Ti.

The result of the ethylene polymerization test (H_2 pressure: 3 atm., C_2H_4 pressure: 10 atm.) is recorded on Table I.

EXAMPLE 3

2.4 g of anhydrous $MgCl_2$ were dissolved in 17 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$ by heating at 140 °C under stirring for 3 hours. The resulting solution was diluted with 45 cc of n-heptane, 95 g of $TiCl_4$ were added thereto in 90 minutes and the mixture was then heated at 98 °C under stirring for 2 hours. The solid product was isolated by filreation, repeatedly washed at room temperature with 50 cc of n-heptane and then dried under vacuum at 40 °C for 3 hours. A catalyst component containing 22.8% of Ti was obtained.

The result of the polymerization test (H_2 pressure: 4 atm., C_2H_4 pressure: 9 atm.) is recorded on Table I.

EXAMPLE 4

2.4 g of anhydrous $MgCl_2$ were dissolved in 17 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$ by heating at 140 °C under stirring for 3 hours.

The solution so obtained was added, after dilution with 45 cc of anhydrous n-hexane, with 19 g of $TiCl_4$ in 90 minutes at room temperature, and the resulting suspension was then heated at 60 °C under stirring for 2 hours. The solid product was separated by filtration at 60 °C and was repeatedly washed with 50 cc of anhydrous n-hexane at room temperature till the disappearance of the chlorine ions from the solvent.

After drying under vacuum at 40 °C for 3 hours, a catalyst component containing 8.6% of Ti was obtained.

The result of the polymerization test (H_2 pressure: 3 atm., C_2H_4 pressure: 10 atm.) is recorded on Table I).

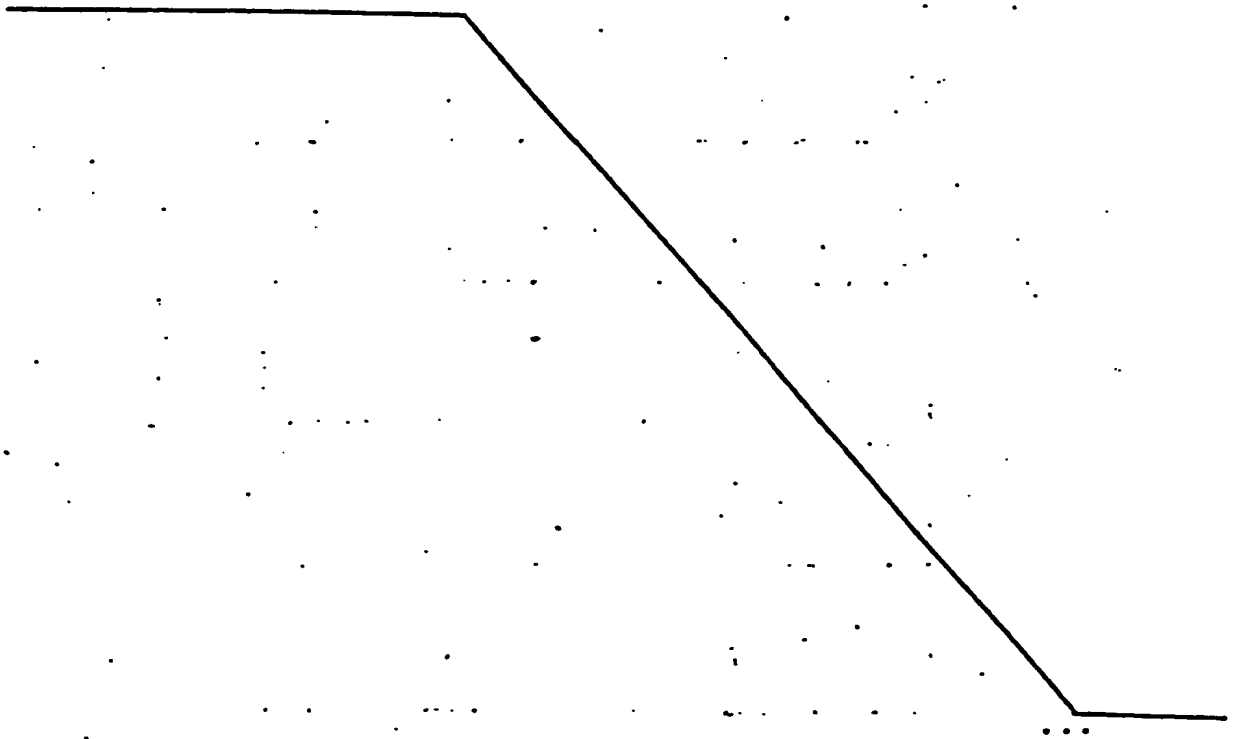

TABLE 1

Silicium-free catalytic components

Example No.	Direct treatment of reaction product (A) + (B) with $TiCl_4$				% of Ti in catalytic component	Polymerization			Polyethylene	
	Diluent cc	$TiCl_4$ g	Temperature °C	Time hours		Catalytic component g	Polymer g	Yield g polym./g Ti	MI E g/10 min.	MI N / MI E
1 *	45 (Isopar G)***	95	135	2	22,3	0,0082	291	160,000	0,09	12,0
2 **	90 (Isopar G)	95	135	2	29,45	0,0080	269	114,000	0,075	13,3
3 *	45 (n-heptane)	95	98	2	22,8	0,0095	342	158,000	0,15	10,5
4 *	45	19	60	2	8,6	0,0080	420	609,000	0,23	9,6

* (A) + (B) : reaction product of 2.4 g of $MgCl_2$ with 17 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$.

** (A) + (B) : reaction product of 4.75 g of $MgCl_2$ with 23.0 g of $Ti(OC_2H_5)_4$.

*** Mixture of isoparaffinic hydrocarbons boiling in the temperature range of from 158° to 172.5°C.

EXAMPLE A

A catalytic component of the type (A) + (B) + silicium compound, like those described in Belgian patent No. 867,400, was prepared from the following reagents:

2.15 g of anhydrous $MgCl_2$

16.6 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$

32 cc of anhydrous n-heptane

12.5 g of $SiCl_4$

8.9 g of PMHS (polymethylhydrosiloxane, produced and sold by Farbenfabriken Bayer with commercial name BAYSILON MH 15).

By operating as indicated in the description it was possible to obtain 10 g of a solid catalytic component containing 15.5% of Ti.

The result of the ethylene polymerization test (H_2 pressure: 5 atm., C_2H_4 pressure : 8 atm.) is recorded on Table II.

EXAMPLE B

A catalytic component was prepared as in example A by employing:

2.2 g of anhydrous $MgCl_2$

17 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$

34 cc of anhydrous n-heptane

38 g of $SiCl_4$

17 g of PMHS.

7 g of a solid catalytic component containing 8.0 g of Ti were obtained.

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The result of the ethylene polymerization test (H_2 pressure: 5 atm., C_2H_4 pressure: 8 atm.) is recorded on Table II.

EXAMPLE C

2.4 g of anhydrous $MgCl_2$ were added to 17 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$ and the mixture was heated at 140 °C for 3 hours, so obtaining a solution which was diluted with 45 cc of n-hexane. 17 g of $SiCl_4$ were added at room temperature to such solution and successively, under stirring, the mixture was heated at 60 °C for 2 hours. The resulting solid product was separated by filtration at 60 °C, it was repeatedly washed with portions of 50 cc of anhydrous n-hexane at room temperature until disappearance of the chlorine ions from the solvent and then it was dried under vacuum at 40 °C for 3 hours. The catalytic component so obtained contained 2.5% of Ti.
The result of the polymerization test (H_2 pressure: 3 atm., C_2H_4 pressure: 10 atm.) is recorded on Table II.

EXAMPLE D

A solution of $MgCl_2$ in $Ti(O\text{-}n\text{-}C_4H_9)_4$, diluted with n-hexane and prepared as described in example C, was additioned with 17 g of polymethylhydrosiloxane at 45°C, under stirring, in 90 minutes; subsequently, in 90 minutes too, 85 g of $SiCl_4$

were added. The suspension so obtained was heated at 60 °C under stirring for 2 hours. By filtering such suspension at 60 °C, a catalytic component was isolated, which was washed and dried as described in example C; its Ti content was of 4.5%.

The result of the polymerization test (H_2 pressure: 3 atm., C_2H_4 pressure: 10 atm.) is recorded on Table II.

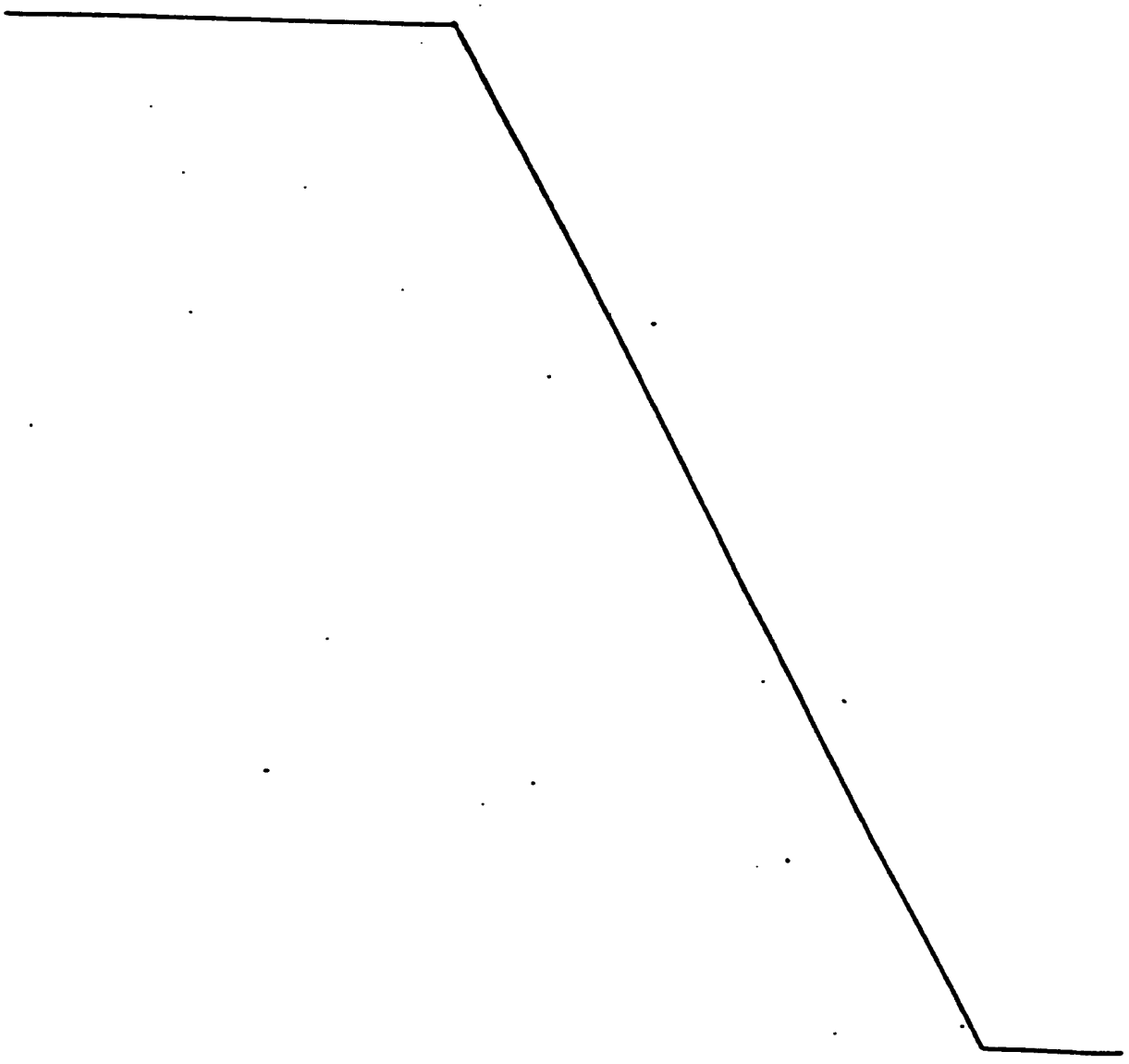

TABLE II

Comparative examples

Example No.	% of Ti in the catalyst component	Polymerization			Polyethylene	
		Catalyst component g	Polymer g	Yield g polym./g Ti	MI E g/10 min.	MI N / MI E
A	15,5	0,0100	279	180,000	0,9	8,0
B	8,0	0,0056	148	330,000	0,85	8,5
C	2,5	0,0097	225	930,000	0,4	8,5
D	4,5	0,0088	226	571,000	0,28	8,4

EXAMPLE 5

10 g of a catalyst component prepared according to example A were suspended in 40 cc of anhydrous n-heptane containing 42 g of $TiCl_4$; the mixture was heated at 98 °C under stirring for 2 hours, then it was allowed to cool to 60 °C and the liquid phase was removed by syphoning. The solid residue was repeatedly washed at room temperature with portions of 50 cc of anhydrous n-hexane until disappearance of the chlorine ions from the solvent, and finally it was dried under vacuum at 40 °C for 3 hours.

The catalytic component so obtained contained 23.0% of Ti.

The result of the ethylene polymerization test(H_2 pressure: 5 atm., C_2H_4 pressure: 8 atm.) is recorded on Table III.

EXAMPLES 6, 7, 8, 9, and 10

Always starting from 10 g of a catalyst component prepared as in example A, other components were prepared as described in example 5, but with the differences indicated on Table III.

The results of the polymerization tests (H_2 pressure: 5 atm., C_2H_4 pressure: 8 atm.) are recorded on the same Table.

EXAMPLE 11

10 g of a catalyst component prepared as in example B were reacted with the amount of $TiCl_4$ and under the conditions as indicated on Table III, obtaining a catalyst component

containing 12.05% of Ti which was used for carrying out the polymerization of ethylene (H_2 pressure: 5 atm., C_2H_4 pressure: 8 atm.).
The result of such test is recorded on Table III.

EXAMPLE 12

10 g of a catalyst component prepared as in example A were suspended in 40 cc of anhydrous n-hexane at room temperature and the resulting suspension was additioned, in 30 minutes and under stirring, with 55 g of $VOCl_3$. The mixture was heated at 68 °C under stirring for 1 hour. At 60 °C, after decantation of the solid product, the liquid phase was removed by syphoning. The solid product was repeatedly washed at room temperature with 50 cc of anhydrous n-hexane and then dried under vacuum at 40°C for 3 hours. A catalyst component was obtained which contained 4.95% of Ti and 21.0% of V.
The result of the polymerization test (H_2 pressure: 5 atm., C_2H_4 pressure: 8 atm.) is recorded on Table III.

EXAMPLE 13

2.4 g of anhydrous $MgCl_2$ were dissolved in 17 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$ by heating at 140 °C under stirring for 3 hours.
The resulting solution was diluted with 45 cc of ISOPAR G

TABLE III

Silicium-containing catalyst components

Example No.	Treatment of intermediate catalytic components (containing silicium)				% of Ti in the catal. component	Polymerization			Polyethylene	
	Diluent cc	$TiCl_4$ g	Temper. °C	Time hours		Catalyst component g	Polymer g	Yield g polym./g Ti	MI E g/10 min.	MI N / MI E
5 *	40 (n-heptane)	42	98	2	23.0	0.0087	200	100,000	0.21	11.5
6 *	40 (n-heptane)	84	98	2	20.2	0.0086	234	135,000	0.39	10.8
7 *		84	60	2	18.8	0.0063	248	210,000	0.61	10.7
8 *		84	100	2	21.35	0.009	160	83,000	0.25	12.5
9 *		84	136	2	23.15	0.010	215	93,000	0.14	11.4
10 *		84	136	5	21.45	0.011	197	84,000	0.09	12.0
11 **		130	136	2	12.05	0.006	188	261,000	0.27	10.7
12 *	40 (n-hexane)	55 $VOCl_3$	68	1	1.95 Ti 21.0 V	0.021	20	19,000	0.065	18.8

continuation of Table III

Example No.	Treatment of intermediate catalytic components (containing silicium)				% of Ti in the catal. component	Polymerization			Polyethylene	
	Diluent cc	$TiCl_4$ g	Temper. °C	Time hours		Catalyst component g	Polymer g	Yield g polym./g Ti	MI E g/10 min.	MI N / MI E
13	45 (Isopar G)	95	135	2	25,75	0,0132	200	59,000	0,12	14,6
14	45 (n-hexane)	95	60	2	25,45	0,0115	235	80,000	0,20	10,6

* 10 g of the catalyst component of example A were employed.

** 10 g of the catalyst component of example B were employed.

WHAT IS CLAIMED IS:

1. Components of catalysts for the polymerization of olefins, comprising the product which is obtained by reacting the reaction product between:

(A) a magnesium compound selected from

1) compounds of formula $X_nMg(OR)_{2-n}$

wherein X is Cl or Br, a group -OH, an alkyl, an aryl or a cycloalkyl having 1 to 20 carbon atoms; R is an alkyl, an aryl or a cycloalkyl having 1 to 20 carbon atoms, or a group -COR' in which R' is a hydrocarbon radical like the ones specified for R; $0 \leq n \leq 2$;

2) compounds of formula R Mg X

wherein X is Cl or Br and R is an alkyl, an aryl or a cycloalkyl having 1 to 20 carbon atoms;

3) MgO, $Mg(OH)_2$, XMgOH, in which X is Cl or Br;

and

(B) a compound of titanium, vanadium or zirconium having at least two metal-oxygen bonds of the type Ti-OR, V-OR or Zr-OR, in which R is an alkyl, an aryl or a cycloalkyl having 1 to 20 carbon atoms or the group $CH_3-\overset{|}{C}=CH-CO-CH_3$,

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containing 12.05% of Ti which was used for carrying out the polymerization of ethylene (H_2 pressure: 5 atm., C_2H_4 pressure: 8 atm.).
The result of such test is recorded on Table III.

EXAMPLE 12

10 g of a catalyst component prepared as in example A were suspended in 40 cc of anhydrous n-hexane at room temperature and the resulting suspension was additioned, in 30 minutes and under stirring, with 55 g of $VOCl_3$. The mixture was heated at 68 °C under stirring for 1 hour. At 60 °C, after decantation of the solid product, the liquid phase was removed by syphoning. The solid product was repeatedly washed at room temperature with 50 cc of anhydrous n-hexane and then dried under vacuum at 40°C for 3 hours. A catalyst component was obtained which contained 4.95% of Ti and 21.0% of V.
The result of the polymerization test (H_2 pressure: 5 atm., C_2H_4 pressure: 8 atm.) is recorded on Table III.

EXAMPLE 13

2.4 g of anhydrous $MgCl_2$ were dissolved in 17 g of $Ti(O\text{-}n\text{-}C_4H_9)_4$ by heating at 140 °C under stirring for 3 hours. The resulting solution was diluted with 45 cc of ISOPAR G

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(a mixture of isoparaffinic hydrocarbons produced by Esso Chemical Co., boiling in the temperature range of from 158° to 172.5 °C) and maintaining said solution at 45 °C and under stirring, 17 g of polymethylhydrosiloxane were added thereto in 90 minutes. The resulting suspension was additioned, always at 45°C, with 95 g of $TiCl_4$ in 90 minutes, whereupon it was reacted at 135 °C under stirring for 2 hours. After cooling to 60 °C, the solid catalytic component so formed was isolated by filtration and it was repeatedly washed, at room temperature, with 50 cc of n-hexane every time.
After drying under vacuum at 40 °C for 3 hours, such catalyst component contained 25.75% of Ti.
The result of the polymerization test (H_2 pressure: 7 atm., C_2H_4 pressure: 6 atm.) is recorded on Table III.

EXAMPLE 14

The solution of $MgCl_2$ in $Ti(O\text{-}n\text{-}C_4H_9)_4$ diluted with n-hexane and prepared as described in example C was additioned, in 90 minutes, at 45°C and under stirring, with 17 g of polymethylhydrosiloxane and successively, always in 90 minutes, with 95 g of $TiCl_4$. The resulting suspension was then heated at 60 °C going on stirring at such temperature for 2 hours. By filtering the suspension at 60 °C a solid catalyst component was isolated which was repeatedly washed with 50 cc of n-he-

with

(C) a halogenated compound of a transition metal of Groups IV, V, VI of the Periodic System of formula MO_mX_n in which M = transition metal, X = Cl or Br, $m \geq 0$, $n > 0$, 2m+n being equal to the valence of metal M.

2) Catalyst components according to claim 1, comprising the product obtained by reacting the product of the reaction between $MgCl_2$ and $Ti(O\text{-}n\text{-}C_4H_9)_4$ with $TiCl_4$.

3) Catalyst components according to claim 1, comprising the product obtained by reaction of $TiCl_4$ with the product of the reaction between $MgCl_2$ and $Ti(OC_2H_5)_4$.

4) Catalyst components according to claim 1, consisting of the product obtained by reacting the product of the reaction between compounds (A) and (B) with a silicium compound showing a halogenating and/or reducing action and then with compound (C).

5) Catalyst components according to claim 4, consisting of the product which is obtained by reacting the product of the reaction between $MgCl_2$ and $Ti(O\text{-}n\text{-}C_4H_9)_4$ with a mixture of $SiCl_4$ and polymethylhydrosiloxane and then with $TiCl_4$.

6) Catalyst components according to claim 4, consisting of the product which is obtained by reacting the product of the reaction between $MgCl_2$ and $Ti(O\text{-}n\text{-}C_4H_9)_4$ with a mixture of $SiCl_4$ and polymethylhydrosiloxane and then with $VOCl_3$.

7) Catalyst components according to claim 4, consisting of the producct which is obtained by reacting the product of the reaction between $MgCl_2$ and $Ti(O\text{-}n\text{-}C_4H_9)_4$ with polymethylhydrosiloxane and then with $TiCl_4$.

8) Catalysts for polymerizing ethylene, consisting of a combination of a catalyst component according to any of claims 1 to 7 hereinbefore and of an aluminium-alkyl compound.

Milan, June 15, 1981

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(71) Applicant: Montedison S.p.A.
31, Foro Buonaparte
I-20121 Milan(IT)

(72) Inventor: Cuffiani, Illaro
33, via Bagaro
Ferrara(IT)

(72) Inventor: Galli, Paolo
106, viale Po
Ferrara(IT)

(72) Inventor: Zucchini, Umberto
11, via Leopardi
Ferrara(IT)

(74) Representative: Zumstein, Fritz, Dr. et al,
Dr. F. Zumstein sen. Dr. E. Assmann Dr. R.
Koenigsberger Dr. F. Zumstein jun. Dipl.-Ing. F.
Klingseisen Bräuhausstrasse 4
D-8000 München 2(DE)

(54) Catalyst components for polymerizing ethylene.

(57) Components of catalysts for polymerizing ethylene and the mixture of ethylene with alpha-olefins comprising the reaction product of (A) a magnesium compound, as Mg-chloride, Mg-alcoholate or a Grignard compound, with (B) a titanium, vanadium or zirconium compound having at least 2 metal-oxygen bonds, as a tetra-alcoholate, and with (C) a halogenated compound of metals of B, as Ti-tetrachloride.

According to an aspect of the invention, the reaction product (A) + (B), before being reacted with (C), is treated with a silicium compound having a halogenating and/or reducing action.

The catalysts according to the invention are suitable for obtaining ethylene polymers having a broad distribution of molecular weights.

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EUROPEAN SEARCH REPORT

0045885

Application number

EP 81 10 5856

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	EP-A-0 007 425 (PHILLIPS PETROLEUM CO.) *Claims 1-10; page 11, lines 12-14, page 13, lines 19-29*	1-3,8	C 08 F 10/02 C 08 F 4/64 C 08 F 4/68 C 08 F 4/02
X	EP-A-0 002 221 (HOECHST) *Claims 1-6; page 3, lines 31-34, page 5, lines 27-35; page 6, lines 11-20; page 7, line 13 - page 8, line 36; page 9, lines 19-31*	1,4,8	
X	FR-A-2 265 768 (SUMITOMO) *Claims 1-13* & GBA 1498862	1,4,8	
D,A	BE-A- 867 400 (MONTEDISON) *Claims 1,13,20-23; example 1* & USA 4218339 (Cat. P)	4-6,8	
A	FR-A-2 147 905 (HOECHST) *Claims 1-14; page 5, lines 21-26* & GBA 1357474	1	TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 08 F 10/00 C 08 F 10/02 C 08 F 10/04 C 08 F 10/06 C 08 F 10/08 C 08 F 10/10 C 08 F 10/12 C 08 F 10/14 C 08 F 110/00 C 08 F 110/02 C 08 F 110/04 C 08 F 110/06 C 08 F 110/08 C 08 F 110/10 C 08 F 110/12 C 08 F 110/14 C 08 F 210/00 C 08 F 210/02
E	EP-A-0 036 660 (PHILLIPS PETROLEUM CG) *Claims 1-10; example*	1,4,8	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-05-1982	WEBER H.

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EP 81 10 5856

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 08 F 210/04 C 08 F 210/06 C 08 F 210/08 C 08 F 210/10 C 08 F 210/12 C 08 F 210/14 C 08 F 210/16 C 08 F 4/64 C 08 F 4/68 C 08 F 4/02

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